



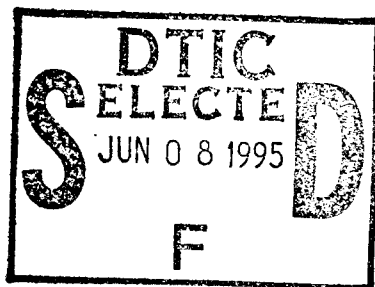
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Miscellaneous Paper EL-95-3
May 1995

Review of Water Quality Monitoring and Recommendations for Water Quality Modeling of the Lower St. Johns River

by Thomas M. Cole



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Prepared for U.S. Army Engineer District, Jacksonville
and St. Johns River Water Management District

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by Thomas M. Cole

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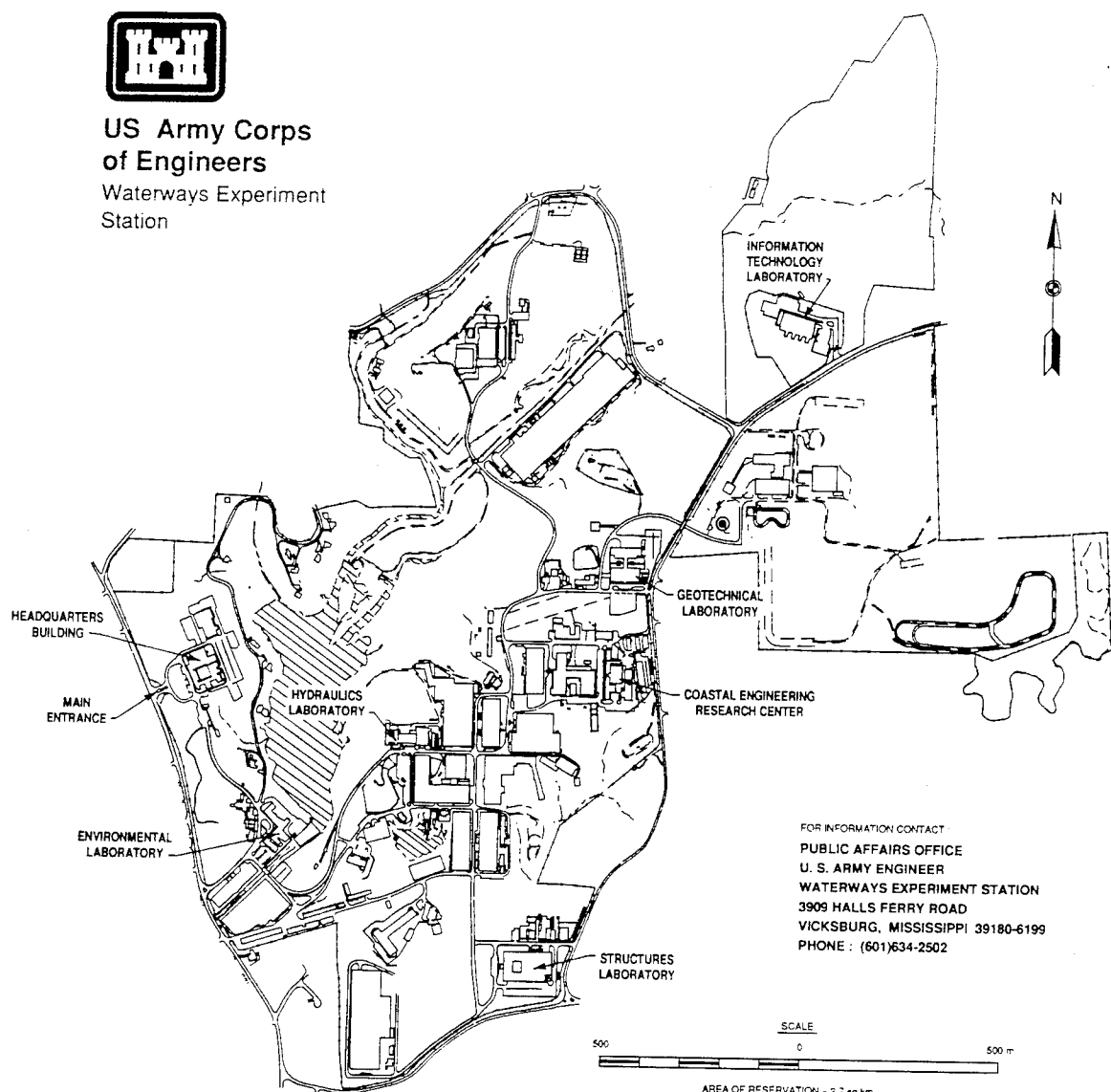
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Preface

This report presents water quality monitoring and modeling recommendations of the Lower St. Johns River. This report was prepared in the Environmental Laboratory (EL), U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The study was sponsored by the U.S. Army Engineer District, Jacksonville, and was funded under the Military Interdepartmental Purchase Request No. RM-CW-92-0161, dated 04 September 1992.

The Principal Investigator of this study was Mr. Thomas M. Cole of the Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Processes and Effects Division (EPED), EL. This report was prepared by Mr. Cole under the direct supervision of Dr. Mark Dortch, Chief, WQCMB, and under the general supervision of Mr. Donald L. Robey, Chief, EPED, and Dr. John W. Keeley, Director, EL. Technical reviews by Dr. Dortch and Ms. Dorothy H. Tillman are gratefully acknowledged.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander of WES was COL Bruce K. Howard, EN.

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Introduction

The St. Johns River Water Management District (SJRWMD) has plans to develop a comprehensive modeling system for the Lower St. Johns River Estuary (LSJRE). The modeling system will be used to provide information for issues concerning watershed management, water supply, pollutant loadings, and eutrophication. Thus, the modeling system will require models of the watershed, hydrodynamics, sediment transport processes, and water quality including algal/nutrient/dissolved oxygen interactions and contaminants. The water quality model is an important component of the system. In light of this, the SJRWMD has requested a review of the present water quality monitoring program to insure that proper and sufficient data are being collected to support future water quality modeling efforts.

This report reviews present water quality data gathering efforts, recommends additional data efforts, and recommends and discusses a water quality model suitable to meet the objectives of the SJRWMD.

Water Quality Monitoring

Data provided by SJRWMD for review were limited in scope. These data included a list of parameters presently sampled by the SJRWMD, sampling station locations used by SJRWMD and other agencies, values of typical water quality parameters plotted spatially from just downstream of the Ocklawaha River to the estuary mouth for one sampling event, and average values from 1983 to 1992 for three sections of the St. Johns River. Therefore, a comprehensive review of existing data is not possible in this report. The following provides a limited discussion of the provided water quality data and discusses in general terms water quality data requirements necessary to support a water quality model of the LSJR.

Existing Monitoring

Sampled Parameters

Table 1 lists the parameters routinely sampled for by SJRWMD. In addition, metals including calcium, magnesium, chromium, zinc, lead, cadmium, and copper are also monitored.

Spatial Monitoring

The SJRWMD has an extensive water quality sampling program in place. Information provided by SJRWMD shows that approximately 40 stations are routinely sampled throughout the Lower St. Johns River by the SJRWMD. Approximately 50 additional stations are sampled by other agencies. No information was supplied as to what water quality parameters were sampled at the additional stations. Major tributaries appear to be adequately represented allowing for development of river loading estimates. No information was provided on the vertical extent of sampling.

Temporal Monitoring

Water quality parameters are typically sampled once a month. In addition, synoptic sampling events the length of the lower river are conducted approximately twice a year. No information was provided as to what parameters are

sampled for during the synoptic events. It is assumed that the parameters include those listed in Table 1.

Table 1 Sampled Water Quality Parameters	
Parameter	Frequency
Temperature	monthly
pH	monthly
Dissolved oxygen	monthly
Ammonium-N	monthly
Nitrate + Nitrite-N	monthly
Total Kjeldahl N	monthly
Total phosphorus	monthly
Orthophosphate	monthly
Dissolved silica	monthly
Total suspended solids	monthly
Total dissolved solids	monthly
Sulfate	monthly
Chloride	monthly
Chlorophyll A,B,C, and phaeophyton	monthly
Total organic carbon	monthly
Alkalinity	monthly
Turbidity	monthly
Color	monthly

Determination of Loadings

A key to any successful water quality modeling effort is an accurate determination of the loadings to the system. Without the correct loadings, calibration of the model is difficult and results of management scenarios will be suspect at best. It is therefore crucial to obtain accurate loading estimates. Stations at tributary mouths are presently sampled monthly. This is not sufficient to determine accurate estimates of tributary loadings. A sampling procedure for estimating loads from tributary loads will be discussed in more detail in the next section.

Recommended Water Quality Monitoring

Table 2 lists the recommended parameters necessary for supporting a state-of-the-art water quality model of the Lower St. Johns River. Of primary importance are particulate (POC) and dissolved organic carbon (DOC), primary production, and sediment oxygen demand and nutrient fluxes. Dissolved organic carbon plays a key role in eutrophication related issues in the LSJR. Based on color measurements and visual inspection of the LSJR, it appears that productivity in the fresh water portion of the river is limited by light penetration due primarily to DOC. Discussions with personnel from SJRWMD suggest that loadings of DOC are primarily from major tributaries and wetland areas in the upper portion of the river. Therefore, it is imperative that accurate regressions of DOC with flow be developed for estimating DOC loadings to the system. Total inorganic carbon, along with pH and alkalinity, will allow modeling of the pH-carbonate system.

Also of importance are determinations of phytoplankton productivity and respiration rates and bioassays for nutrient limitations. Water quality models are capable of computing nutrient and light limitations and bioassays would be helpful in comparing model predictions. Productivity and respiration rates are necessary for accurate characterization of carbon assimilation by phytoplankton.

It is also critical to obtain accurate estimates of sediment oxygen demand and nutrient fluxes for proper calibration of a sediment model or for proper specification of boundary values if a sediment model is not used. In addition, proper characterization of the sediments including particulate organic carbon, phosphorus, nitrogen, and inorganic phosphorus is necessary for sediment model calibration.

Total carbon, nitrogen, phosphorus, and silica are necessary to insure that loadings during model calibration are correctly accounted for. Care should be taken during analysis so that no single component is greater than the total nutrient. If this occurs, samples should be immediately analyzed again.

Monthly sampling frequency for all in-pool parameters is generally sufficient in the early stages of a sampling program. However, as knowledge of the system behavior increases, sampling frequency during the most dynamic periods may have to be increased to better capture the dynamics of the system. For example, it may be necessary to sample more frequently during shifts in phytoplankton assemblages in order to gain a better understanding of phytoplankton succession. It is critical to have an understanding of the system in order to accurately represent the processes during a modeling effort. In addition, most modeling studies give direction to future sampling efforts by pinpointing deficiencies in the existing data.

Concerning contaminant modeling, it is hard to make specific recommendations without knowing the contaminant of concern. However, the following param-

Table 2 Recommended Monitoring Parameters	
Water Column	
Temperature	Dissolved phosphate
Salinity	Particulate inorganic phosphorus *
Light extinction	Dissolved organic phosphorus *
Dissolved oxygen	Particulate organic phosphorus *
Ammonium	Total phosphorus *
Nitrate_nitrite	Dissolved silica
Dissolved organic nitrogen *	Particulate biogenic silica *
Particulate organic nitrogen *	Total silica *
Total Nitrogen *	Chlorophyll
pH	Total inorganic carbon *
Alkalinity	
Sediments	
Particulate organic carbon *	Particulate inorganic phosphorus *
Particulate organic nitrogen *	Particulate organic phosphorus *
Processes/Fluxes	
Primary production *	Sediment nitrate flux *
Respiration *	Sediment phosphorus flux *
Sediment oxygen demand *	Sediment silica flux *
Sediment ammonium flux *	Sediment COD flux *
Nutrient limitation bioassays *	
* recommended additional sampling and analyses	

ters should be measured for any contaminant modeling study. In the sediments, bulk and dry density, grain size, TOC and DOC, longterm burial velocities, and contaminant concentrations should be measured. Longterm burial rates are typically determined from strontium core datings. In the water column, total and dissolved contaminant concentrations, TOC and DOC, and settling velocity should be measured. In addition, sorption and degradation values should be determined from either the literature or from laboratory experiments.

Water Quality Modeling

Recommended Water Quality Model

The recognized state-of-the-art water quality model with respect to eutrophication related issues is CE-QUAL-ICM (Cerco and Cole, 1993). The model is similar in concept to WASP (Ambrose, et.al., 1986) and was developed over the last six years by the Water Quality and Contaminant Modeling Branch at Waterways Experiment Station for application to Chesapeake Bay. The model is presently being used by the U.S. Army Engineer Waterways Experiment Station (WES) to evaluate the effectiveness of nutrient reduction strategies on eutrophication in the Bay, and has also been used to address management issues in the New York Bight, Indian River-Reheboth Bay, Delaware, LA Long Beach, and Lower Green Bay. CE-QUAL-ICM is the first 3-D water quality model shown to be capable of addressing water quality issues spanning multiple decades.

Capabilities

Mass Balance. Water quality modeling can be viewed simply as mass-balance modeling wherein the model keeps track of constituent mass over time as it is affected by external boundary conditions and internal kinetic transformations. CE-QUAL-ICM has been shown to account for constituent mass within the accuracy of a given computer. This is the most fundamental requirement of any water quality model - the water quality transformations and numerical solution scheme must maintain mass balances.

Hydrodynamic Linkage. CE-QUAL-ICM is a finite-volume model. Theoretically, the model can link to hydrodynamic models of any dimension or combination of dimensions using either structured or unstructured grids. However, certain numerical solution techniques in the model complicate the linkage to unstructured grid, hydrodynamic models. This will be discussed in more detail in the **Limitations** section.

Transport. CE-QUAL-ICM is a stand alone water quality code decoupled from the hydrodynamics. Output, specifically flows and diffusivities across cell faces, from a chosen hydrodynamic model is used to drive the transport processes. Diffusivities can be optionally specified in the water quality model.

The model is capable of addressing long-term water quality issues in one, two, or three dimensions, or in any combination. Thus, a variety of hydrodynamic models can be used to provide transport information required by CE-QUAL-ICM.

A major advancement incorporated in the model is a subcomponent which calculates residual currents from the hydrodynamic model averaged over a given time period (typically a tidal cycle). This allows for longer timesteps in the water quality model while still maintaining the transport properties of the hydrodynamic model and contributes to the model's ability to perform longterm simulations. The calculation of residual currents is presently incorporated into the hydrodynamic model CH3D (Dortch, 1992). Additional effort would be required to provide residual flows from a different hydrodynamic model.

Another important advancement incorporated into CE-QUAL-ICM is a higher-order numerical transport scheme, QUICKEST (Leonard, 1979), which greatly reduces numerical diffusion during constituent transport. It is well known that upwind differencing produces numerical dispersion which can often be much greater than the physical dispersion. Because of numerical dispersion, upwind differencing cannot resolve sharp gradients which are typically encountered when modeling water quality. The transport solution scheme in CE-QUAL-ICM can use either upwind differencing or QUICKEST. The preferred method is QUICKEST. The Chesapeake Bay Study showed that observed vertical gradients in salinity could not be reproduced in the hydrodynamic model without the inclusion of a higher-order transport scheme (Johnson, 1991).

Vertical transport is differentiated from horizontal transport in the model. Vertical diffusion is always handled implicitly in time which removes vertical diffusion from numerical stability criteria. Vertical advection employs a time-weighted scheme which can vary between fully explicit, fully implicit, or a combination of the two. The fully implicit option also eliminates vertical advection from the transport stability criteria. The combination of fully implicit vertical advection and diffusion contributes to the model's ability to conduct longterm simulations (ie., decades) required when evaluating nutrient reduction scenarios or contaminant modeling.

The model also includes an algorithm which adjusts the timestep based on estimates of numerical stability criteria required by the numerical solution of the advection-diffusion equation. Thus, the timestep automatically decreases during periods of high constituent fluxes and increases during low periods. Previously, the timestep in most water quality models was set to the lowest value encountered during a simulation to maintain numerical stability. Automatic model adjustment of the timestep is referred to as autosteping and has a dramatic effect on reducing the computational requirements of the model.

Eutrophication Interactions. The model contains a full suite of water quality constituents used to address eutrophication related issues. A complete description of the state variables and their interactions is given in Appendix A. This

appendix is provided primarily to allow the reader to determine if the important processes and proper formulations for the LSJR are included in the model. This appendix was taken from a draft report of the Chesapeake Bay study (Cercio and Cole, 1993).

Sediment Submodel. CE-QUAL-ICM contains a predictive sediment submodel which represents the accumulation and decay or diagenesis of organic matter in the sediments and its effect on water column oxygen demand and nutrient fluxes from the sediments (DiToro and Fitzpatrick, 1993). The present sediment formulation is applicable mainly to saline conditions in the water column. A freshwater formulation which includes iron and manganese will be incorporated into the model in the future.

Limitations. It was previously stated that CE-QUAL-ICM is the state-of-the-art in water quality modeling. However, it does not contain all of the state-of-the-art capabilities available today in the field of water quality modeling. It should be noted that no other water quality model contains complete state-of-the-art capabilities either. The model was initially developed to address specific management issues for the Chesapeake Bay Study, but the coding of the model is such that additional capabilities can be incorporated as needed. In addition, the algorithms in the code are applicable but not specific to Chesapeake Bay.

Experience has shown that nearly every new application of any water quality model requires inclusion of additional processes or reformulation of existing processes to adequately reproduce prototype behavior. CE-QUAL-ICM will evolve over time as new applications require additional capabilities or reformulations. The most important limitations of the model are discussed below.

Hydrodynamic Linkage. The only hydrodynamic model used to drive the transport processes in previous CE-QUAL-ICM applications is CH3D-WES (Johnson, 1991). CH3D-WES is discussed in the companion report and will be discussed only briefly in this report. The discretization grid is boundary fitted, curvilinear, structured, and space staggered. The vertical grid can be either sigma-stretched where the number of layers in the grid are fixed and layer thicknesses vary temporally throughout the water column, or a Z-grid representation where only the surface layer varies in thickness over time. CE-QUAL-ICM is capable of linking to either vertical grid. Most importantly, the higher-order transport scheme in CE-QUAL-ICM requires a structured grid representation. CH3D meets this requirement.

Theoretically, finite-element hydrodynamic models using unstructured grids can be used to drive the transport processes in CE-QUAL-ICM. However, finite-element, unstructured grids have not previously been used with CE-QUAL-ICM. Plans have been made to incorporate the ability to link CE-QUAL-ICM to unstructured grids, but it must be emphasized that research would be involved in linking the water quality model to a finite-element, hydrodynamic model. The following considerations are involved with linking CE-QUAL-ICM to a finite-element hydrodynamic model.

Finite-element hydrodynamic models conserve mass globally, but do not conserve mass locally. As stated previously, the fundamental principle in water quality modeling involves keeping track of constituent mass through external boundary interactions and internal kinetic transformations. Presently, it is not known what affect the inability of a hydrodynamic model to locally conserve mass will have on the ability of CE-QUAL-ICM to reproduce behavior in the prototype. It is believed that finite-element hydrodynamic models can be corrected to conserve mass locally, but, as stated previously, research would be required to establish this.

More importantly, the present higher-order transport scheme (QUICKEST) in CE-QUAL-ICM requires three spatial points to interpolate constituent fluxes across cell faces. Linking CE-QUAL-ICM to an unstructured hydrodynamic model would require the development of a two-point, higher-order transport scheme since the three points required by the present scheme would not be readily discernable. Such schemes are available, but again, research would be involved in implementing the two-point, higher-order transport scheme. Additionally, the new transport scheme must be shown to reproduce the transportive properties of the hydrodynamic solution scheme.

Future Capabilities

Numerous improvements to CE-QUAL-ICM are planned in the future. They are discussed in the following sections.

Sediment Submodel w/ Iron and Manganese Kinetics. The current sediment model was developed to compute carbon diagenesis and sediment-water column fluxes for Chesapeake Bay which is predominately saltwater. Development is underway to make the sediment submodel applicable to freshwater sediments. The main differences between the freshwater and saltwater formulations are that sulfides are the primary source of oxygen demand in saltwater and methane, iron, and manganese along with sulfides are the primary sources of sediment oxygen demand in freshwater.

Carbonate-pH System. A carbonate-pH system with non-conservative alkalinity is being incorporated into the model. A fully tested system is expected by 1995.

Zooplankton. The initial water quality formulations in CE-QUAL-ICM explicitly included the effects of zooplankton by their inclusion as state variables. During model calibration, zooplankton were removed from the formulations and their effects were included in the algal mortality and nutrient recycling terms. Plans are to reintroduce zooplankton into the model as state variables for Phase 2 of the Chesapeake Bay Study.

Macrophytes. Macrophyte/nutrient interactions are not presently included in CE-QUAL-ICM. Phase 2 of the Chesapeake Bay Study will incorporate macrophytes as a state variable. This is presently an active area of research in the modeling community and improvements will be incorporated in the future as a better understanding of the processes are gained.

Contaminants. The contaminant components of the EPA's WASP model (Ambrose, et. al., 1986) are presently being incorporated into the model. No contaminant studies have been conducted with CE-QUAL-ICM; however, a water quality and contaminant modeling study of San Diego Bay is scheduled to start in 1994.

Sediment Transport. Sediment transport is presently not in the model. It should be relatively easy to incorporate sediment transport given sediment transport output from an appropriate hydrodynamic model. Again, sediment transport will probably be incorporated into the model during the San Diego Bay study.

Pre- and Postprocessors. One of the most serious shortcomings of CE-QUAL-ICM is a lack of integrated pre- and postprocessors. Presently, the development of input files requires a hodgepodge of FORTRAN programs whose workings are largely undocumented. The same is true for postprocessing of output. Graphical display of model output consists of a series of FORTRAN programs which use high level graphics subroutine calls from a commercial package called DISSPLA. There are plans to develop integrated processors based on a graphical user interface. However, given the current level of funding, development will take several years to complete.

Computer Requirements

Hardware. CE-QUAL-ICM has previously been run on 80386/80486 PC's, RISC workstations, and a Cray Y-MP and C-90. All of the code development for Chesapeake Bay was performed on a 25 Mhz 80386 PC while model calibration and scenario runs were performed on a Cray Y-MP. Given the rapid advancements in the state-of-the-art in hardware for computationally intensive floating-point code, it is hard to estimate future hardware requirements for management scenarios. It is almost a certainty that the model will run in a reasonable time on workstations costing less than 10K in five years.

Software. Present software requirements are a FORTRAN compiler and a commercial software package called DISSPLA for processing of model output. For PC's, the compiler must be capable of addressing 32-bits in DOS's protected mode. The trend in workstations is toward 64-bit CPU's which deliver the same precision as Cray supercomputers. Machines with 64-bits of precision are not a requirement of the model, but they increase the accuracy of the computations.

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Appendix A

CE-QUAL-ICM Kinetics

The central issues in the water quality model are primary production of carbon by algae and dissolved oxygen concentrations. Primary production provides the energy required by the ecosystem to function. Excessive primary production is detrimental since its decomposition in the water and sediments consumes oxygen. Dissolved oxygen is necessary to support the life functions of higher organisms and is considered an indicator of the "health" of estuarine systems. In order to predict primary production and dissolved oxygen, a large suite of model state variables is necessary (Table A-1).

Table A-1 Water Quality Model State Variables	
temperature	Salinity
total active metal	cyanobacteria
diatoms	green algae
dissolved organic carbon	labile particulate organic carbon
refractory particulate organic carbon	ammonium
nitrate	dissolved organic nitrogen
labile particulate organic nitrogen	refractory particulate organic nitrogen
total phosphate	dissolved organic phosphorus
labile particulate organic phosphorus	refractory particulate organic phosphorus
chemical oxygen demand	dissolved oxygen
particulate biogenic silica	available silica

Conservation Of Mass Equation

The foundation of CE-QUAL-ICM is the solution to the three-dimensional mass-conservation equation for a control volume. The control-volume approach was selected to allow maximum flexibility in linking CE-QUAL-ICM to alternate hydrodynamic models. For each state variable, the conservation of mass is:

$$\frac{\delta V_i C_i}{\delta t} = \sum_{j=1}^n Q_j C_j^* + \sum_{j=1}^n A_j D_j \frac{\delta C}{\delta x_j} + \sum S_i \quad (\text{A-1})$$

where

- V_i = volume (m^3)
- C_i = concentration (g m^{-3})
- Q_j = volumetric flow across flow face j ($\text{m}^3 \text{sec}^{-1}$)
- C_j^* = concentration in flow across flow face j (g m^{-3})
- A_j = area of flow face j (m^2)
- D_j = diffusion coefficient at flow face j ($\text{m}^2 \text{sec}^{-1}$)
- n = number of flow faces attached to control volume
- S_i = control volume external loads and kinetic sources/sinks (g sec^{-1})
- t, x = temporal and spatial coordinates

Solution to the mass-conservation equation uses the QUICKEST finite difference algorithm (Leonard, 1979) for horizontal advection and diffusion and a Crank-Nicolson scheme for vertical advection and diffusion.

State Variables

Algae

Algae are grouped into three model classes: cyanobacteria, diatoms, and greens. The grouping is based upon the distinctive characteristics of each class and upon the significant role they play in the ecosystem. Cyanobacteria, commonly called blue-green algae, are characterized by their abundance (as picoplankton) in saline water and by their bloom-forming characteristics in fresh water. Cyanobacteria are unique in that some species fix atmospheric nitrogen. The cyanobacteria in the model are bloom-forming species that do not fix nitrogen. They are characterized as having negligible settling velocity and subject to low predation pressure. Diatoms are distinguished by their requirement of silica as a nutrient to form cell walls with high settling velocities. Settling of spring diatom blooms to the sediments may be a significant source of carbon for sedi-

ment oxygen demand. Algae that do not fall into the preceding two groups are lumped into the heading of green algae. Green algae settle at a rate intermediate between cyanobacteria and diatoms and are subject to greater grazing pressure than cyanobacteria.

Organic Carbon

Three organic carbon state variables are included: dissolved, labile particulate, and refractory particulate. Labile and refractory distinctions are based upon the time scale of decomposition. Labile organic carbon decomposes on a time scale of days to weeks while refractory organic carbon requires more time. Labile organic carbon decomposes rapidly in the water column or the sediments. Refractory organic carbon decomposes slowly, primarily in the sediments, and contributes to sediment oxygen demand years after deposition.

Nitrogen

Nitrogen is divided into organic and mineral fractions. Organic nitrogen state variables are: dissolved organic nitrogen, labile particulate organic nitrogen, and refractory particulate organic nitrogen. Two mineral nitrogen forms are modeled - ammonium and nitrate/nitrite. Both forms are available for algal nutrient requirements although ammonium is preferred from thermodynamic considerations. The primary reason for distinguishing the two is that ammonium is oxidized by nitrifying bacteria into nitrate. This oxidation can be a significant sink of oxygen in the water column and sediments. An intermediate in the complete oxidation of ammonium, nitrite, also exists. Nitrite concentrations are usually much less than nitrate and, for modeling purposes, are combined with nitrate. The nitrate state variable represents the sum of nitrate plus nitrite.

Phosphorus

As with carbon and nitrogen, organic phosphorus is considered in three states: dissolved, labile particulate, and refractory particulate. Only a single mineral form, total phosphate, is considered. Total phosphate exists in several states within the model: dissolved phosphate, phosphate sorbed to inorganic solids, and phosphate incorporated in algal cells. Equilibrium partition coefficients are used to distribute the total among the three states.

Silica

Silica is divided into two state variables: available silica and particulate biogenic silica. Available silica is primarily dissolved and can be used by diatoms. Particulate biogenic silica cannot be used. In the model, particulate biogenic silica is produced through diatom mortality. Particulate biogenic silica undergoes dissolution to available silica or settles to the bottom sediments.

Chemical Oxygen Demand

Chemical oxygen demand is modeled as the concentration of reduced substances that are oxidizable by inorganic means. The primary component of chemical oxygen demand is sulfide released from sediments. Oxidation of sulfide to sulfate may remove substantial quantities of dissolved oxygen from the water column.

Dissolved Oxygen

Dissolved oxygen is required for the existence of higher life forms. Oxygen availability determines the distribution of organisms and the flow of energy and nutrients in an ecosystem. Dissolved oxygen is a central component of the water quality model.

Total Active Metal

Both phosphate and dissolved silica sorb to inorganic solids - primarily iron and manganese. Sorption and subsequent settling is one pathway for removal of phosphate and silica from the water column. The sediment model does not include iron and manganese. Instead, total active metal is defined as the total concentration of metals that are active in phosphate and silica adsorption and transport. Total active metal is partitioned between particulate and dissolved phases by an oxygen-dependent partition coefficient.

Salinity

Salinity is a conservative tracer that provides verification of the transport component of the model and facilitates examination of conservation of mass. Salinity also influences the dissolved oxygen saturation concentration and is used in the determination of kinetics constants that differ in saline and fresh water.

Temperature

Biochemical reactions are a function of temperature. Reaction rates increase with increasing temperature. Extreme temperatures cause algal mortality.

Kinetic Formulations

The remainder of this appendix details the kinetics of the mass-conservation equation for each state variable. Parameters are defined where they first appear. For consistency with reported rate coefficients, kinetic reactions are defined with a temporal dimension of days. Within the CE-QUAL-ICM code, kinetics sources and sinks rates are converted to seconds for the mass-conservation equation.

Algae

Algae play a central role in the carbon and nutrient cycles. Equations governing the three algal groups are similar with differences among groups expressed through the magnitudes of coefficients in the equations. The letter "x" is used as a "wild card" in the equations and is replaced with a letter that indicates a specific algal group. Algal groups are indicated by:

c = cyanobacteria
d = diatoms
g = green algae

Sources and sinks of algae are:

Growth (production)
Basal metabolism
Predation
Settling

The governing equation for algal biomass is:

$$\frac{\delta}{\delta t} B_x = \left[P_x - B M_x - P R_x - W S_x \frac{\delta}{\delta z} \right] B_x \quad (A-2)$$

where

B_x = algal biomass, expressed as carbon (g C m⁻³)

P_x = production (day^{-1})
 BM_x = basal metabolism (day^{-1})
 PR_x = predation (day^{-1})
 WS_x = settling velocity (m day^{-1})
 z = vertical coordinate (m)

Production. Production by phytoplankton is determined by nutrient availability, light intensity, and temperature. The effects are considered to be multiplicative:

$$P_x = PM_x f(N) f(I) f(T) \quad (\text{A-3})$$

where

PM_x = production under optimal conditions (day^{-1})
 $f(N)$ = effect of suboptimal nutrient concentration ($0 \leq f \leq 1$)
 $f(I)$ = effect of suboptimal illumination ($0 \leq f \leq 1$)
 $f(T)$ = effect of suboptimal temperature ($0 \leq f \leq 1$)

Cyanobacteria are treated as freshwater organisms that undergo rapid mortality in salt water. This effect is included by a salinity toxicity term in the cyanobacteria production equation:

$$P_c = PM_c f(N) f(I) f(T) f(S) \quad (\text{A-4})$$

where

$f(S)$ = salinity effect on cyanobacteria production ($0 \leq f \leq 1$)

Nutrients. Carbon, nitrogen, and phosphorus are the primary nutrients required for algal growth. Diatoms also require silica. Inorganic carbon limitation is not considered in the model. The effects of the remaining nutrients on growth are described by Monod kinetics (Monod, 1949). In this formulation, growth is dependent upon nutrient availability at low nutrient concentrations but is independent of nutrients at high concentrations. A key parameter in the formulation is the half-saturation concentration. In this formulation, the growth rate is half the maximum when available nutrient concentration equals the half-saturation concentration. Liebig's "law of the minimum" (Odum, 1971) states that growth is determined by the nutrient in least supply. For cyanobacteria and greens:

$$f(N) = \text{minimum} \left[\frac{NH_4 + NO_3}{KH_{nx} + NH_4 + NO_3}, \frac{PO_4d}{KH_{px} + PO_4d} \right] \quad (A-5)$$

where

- NH₄ = ammonium concentration (g N m⁻³)
- NO₃ = nitrate concentration (g N m⁻³)
- KH_{nx} = nitrogen uptake half-saturation constant (g N m⁻³)
- PO₄d = dissolved phosphate concentration (g P m⁻³)
- KH_{px} = phosphorus uptake half-saturation constant (g P m⁻³)

Some cyanobacteria, notably the bloom-forming genus *Anabaena*, utilize atmospheric nitrogen to supply nitrogen requirements. In the model, a non-nitrogen fixing algae is considered the predominant cyanobacteria. The potential growth of nitrogen fixers, such as *Anabaena*, can be estimated by removing the nitrogen limitation on cyanobacteria.

Diatoms require silica as well as nitrogen and phosphorus for growth. For diatoms, the nutrient limitation is the minimum of the limitations expressed in Equation A-5 or the following:

$$f(N) = \frac{SAd}{KH_s + SAd} \quad (A-6)$$

where

- SAd = dissolved available silica concentration (g Si m⁻³)
- KH_s = silica half-saturation constant for uptake by diatoms (g Si m⁻³)

Light. Algal production increases as a function of light intensity until an optimal intensity is reached. Beyond the optimal intensity, production declines as intensity increases. Steele's equation (DiToro, et al., 1971) describes this phenomenon:

$$f(I) = \frac{I}{I_s} e^{1 - \frac{I}{I_s}} \quad (A-7)$$

where

- I = illumination rate (Langley's day⁻¹)
- I_s = optimal illumination (Langley's day⁻¹)

Steele's equation describes the instantaneous light limitation at a point in space. However, the model computes limitation integrated over discrete time intervals and aggregated spatially by model segments. In the model, Steele's equation is integrated over one day and is averaged over the thickness of each model segment. This interval does not preclude computation steps less than a day but frees the model from accounting for illumination in "real time." Daily averaging precludes computation of diurnal fluctuations in algal production. This restriction is not severe since the equations for algal growth are not appropriate for short time scales.

Assuming light intensity declines exponentially with depth, the integrated, averaged form of Steele's equation is:

$$f(I) = \frac{2.72 FD}{K_{ess} \Delta z} (e^{\alpha b} - e^{\alpha t}) \quad (A-8)$$

$$\alpha b = - \frac{I_0}{FD I_s} e^{-K_{ess}(ZD + \Delta z)} \quad (A-9)$$

$$\alpha t = - \frac{I_0}{FD I_s} e^{-K_{ess} ZD} \quad (A-10)$$

where

- I_0 = daily illumination at water surface (Langley's day⁻¹)
- FD = fractional daylength ($0 \leq FD \leq 1$)
- K_{ess} = total light attenuation coefficient (m⁻¹)
- Δz = model segment thickness (m)
- ZD = distance from water surface to top of model segment (m)

Light attenuation in the water column is composed of two fractions: a background value dependent on water color and concentration of suspended particles, and extinction due to light absorption by chlorophyll:

$$K_{ess} = K_{eb} + K_{chl} \sum_{x=c,d,g} \frac{1}{CChlx} B_x \quad (A-11)$$

where

- K_{eb} = background light attenuation (m⁻¹)
- K_{chl} = chlorophyll 'a' light attenuation coefficient (m² mg⁻¹)
- $CChlx$ = algal group x carbon-to-chlorophyll ratio (g C mg⁻¹ chl)

Optimal illumination for photosynthesis depends on algal taxonomy, duration of exposure, temperature, nutrient status, and previous acclimation. Variations in optimal illumination are largely due to adaptations by algae intended to maximize production in a variable environment. Steele (1962) noted the result of adaptations is that optimal illumination is a consistent fraction ($\approx 50\%$) of daily illumination. Kremer and Nixon (1978) reported an analogous finding that maximum algal production occurs at a constant depth ($\approx 1\text{m}$) in the water column. Their approach is adopted here so that optimal illumination is expressed:

$$I_{sx} = I_{oavg} e^{-K_{ess} D_{optx}} \quad (A-12)$$

where

I_{oavg} = adjusted surface illumination (Langley's day⁻¹)
 D_{optx} = maximum algal production depth (m)

A minimum, I_{smin} , is specified for optimal illumination so that algae do not thrive at extremely low light levels. The time required for algae to adapt to changes in illumination is accounted for by computing I_s based on a time-weighted average of daily illumination:

$$I_{oavg} = 0.7 I_o + 0.2 I_1 + 0.1 I_2 \quad (A-13)$$

where

I_1 = daily illumination one day preceding model day (Langley's day⁻¹)
 I_2 = daily illumination two days preceding model day
 (Langley's day⁻¹)

Temperature. Algal production increases as a function of temperature until an optimum temperature is reached. Above the optimum, production declines until a lethal temperature is reached. Numerous functional representations of temperature effects are available. Inspection of growth versus temperature curves indicates a function similar to a Gaussian probability curve provides a good fit to observations:

$$\begin{aligned} f(T) &= e^{-KT_{gx1}(T - T_{mx})^2} \text{ when } T \leq T_{mx} \\ &= e^{-KT_{gx2}(T_{mx} - T)^2} \text{ when } T > T_{mx} \end{aligned} \quad (A-14)$$

where

- T = temperature (C°)
- Tmx = optimal temperature for algal growth (C°)
- KTgx1 = temperature effect below TMx on growth (C°⁻²)
- KTgx2 = temperature effect above TMx on growth (C°⁻²)

Salinity Toxicity. The effect of salinity on freshwater cyanobacteria is represented by an empirical equation:

$$f(S) = \frac{Stox^2}{Stox^2 + S^2} \quad (A-15)$$

where

Stox = salinity which *Microcystis* growth is halved (ppt)

Settling. In late winter and early spring, diatom populations are assumed to be characterized by large species with high settling velocities. At the end of spring, large diatoms are assumed to be replaced by populations of smaller individuals with lower settling velocities. Diatom settling is represented in the model as:

$$WSd = WSdb + Prdval \cdot WSds \quad (A-16)$$

where

- WSdb = base diatom settling velocity (m day⁻¹)
- WSds = large diatoms enhanced settling velocity (m day⁻¹)
- Prdval = piecewise function used to specify seasonal diatom settling velocity

Basal Metabolism. In the model, basal metabolism is the sum of all internal processes that decrease algal biomass. A portion of metabolism is respiration which may be viewed as a reversal of production. In respiration, carbon and nutrients are returned to the environment accompanied by the consumption of dissolved oxygen. A second internal sink of biomass is the excretion of dissolved organic carbon.

Respiration cannot proceed in the absence of oxygen. Basal metabolism cannot decrease in proportion to oxygen availability or algae would approach immortality under anoxic conditions. To solve this dilemma, basal metabolism is considered to be independent of dissolved oxygen concentration but the distribution

of metabolism between respiration and excretion is oxygen-dependent. When oxygen is freely available, respiration is a large fraction of the total. When oxygen is restricted, excretion becomes dominant. Formulation of this process is detailed in the text that describes algal effects on carbon and dissolved oxygen.

Basal metabolism is commonly considered to be an exponentially increasing function of temperature:

$$BM_x = BM_{rx} e^{KT_{bx} (T - T_{rx})} \quad (A-17)$$

where

- BM_{rx} = metabolic rate at T_{rx} (day^{-1})
- KT_{bx} = temperature effect on metabolism ($^{\circ}\text{C}^{-1}$)
- T_{rx} = reference temperature for metabolism ($^{\circ}\text{C}$)

Predation. Detailed specification of predation rates requires predictive modeling of zooplankton biomass and activity. At present, zooplankton are not included in the model. Consequently, a constant predation rate is specified. The present formulation assumes zooplankton biomass is a constant fraction of algal biomass. Zooplankton activity is assumed to be influenced by temperature and is taken into account by incorporating an exponential temperature relationship into the predation term. The predation formulation is identical to basal metabolism. The difference in predation and basal metabolism lies in the distribution of the end products of these processes:

$$PR_x = BPR_x e^{KT_{bx} (T - T_{rx})} \quad (A-18)$$

where

- BPR_x = predation rate at T_{rx} (day^{-1})

Effect of Algae on Organic Carbon. During production and respiration, algae primarily take up and produce carbon dioxide, an inorganic form not considered in the model. A small fraction of basal metabolism is exuded as dissolved organic carbon. In the model, this fraction increases as dissolved oxygen becomes scarce. Algae also produce organic carbon through the effects of predation. Zooplankton take up and redistribute algal carbon through grazing, assimilation, respiration, and excretion. Since zooplankton are not included in the model, routing of algal carbon through zooplankton is simulated by empiri-

cal distribution coefficients. The effects of algae on organic carbon are expressed as:

$$\frac{\delta}{\delta t} \text{DOC} = \left[\left(\text{FCDx} + (1 - \text{FCDx}) \frac{\text{KHrx}}{\text{KHrx} + \text{DO}} \right) \text{BMx} + \text{FCDP PRx} \right] \text{Bx} \quad (\text{A-19})$$

$$\frac{\delta}{\delta t} \text{LPOC} = \text{FCLP PRx Bx} \quad (\text{A-20})$$

$$\frac{\delta}{\delta t} \text{RPOC} = \text{FCRP PRx Bx} \quad (\text{A-21})$$

where

- DOC = dissolved organic carbon concentration (g C m⁻³)
- DO = dissolved oxygen concentration (g O₂ m⁻³)
- LPOC = labile particulate organic carbon concentration (g C m⁻³)
- RPOC = refractory particulate organic carbon concentration (g C m⁻³)
- FCDx = fraction of basal metabolism exuded as dissolved organic carbon
- KHrx = half-saturation concentration for algal dissolved organic carbon excretion (g O₂ m⁻³)
- FCDP = fraction of dissolved organic carbon produced by predation
- FCLP = fraction of labile particulate carbon produced by predation
- FCRP = fraction of refractory particulate carbon produced by predation

The sum of the three predation fractions must equal unity.

Effect of Algae on Phosphorus. Algae take up dissolved phosphate during production and release dissolved phosphate and organic phosphorus through mortality. As with carbon, the fate of algal phosphorus released by metabolism and predation is represented by distribution coefficients. Since the total phosphate state variable includes both intra- and extracellular phosphate, no explicit representation of the effects of algae on phosphate is necessary. Distribution of total phosphate is determined by partition coefficients as detailed in the "PHOSPHORUS" section of this appendix. The equations that express the effects of algae on organic phosphorus are:

$$\frac{\delta}{\delta t} \text{DOP} = (\text{BMx FPDx} + \text{PRx FPDp}) \text{APC Bx} \quad (\text{A-22})$$

$$\frac{\delta}{\delta t} \text{LPOP} = (\text{BM}_x \text{FPL}_x + \text{PR}_x \text{FPLP}) \text{APC B}_x \quad (\text{A-23})$$

$$\frac{\delta}{\delta t} \text{RPOP} = (\text{BM}_x \text{FPR}_x + \text{PR}_x \text{FPRP}) \text{APC B}_x \quad (\text{A-24})$$

where

- DOP = dissolved organic phosphorus (g P m⁻³)
- LPOP = labile particulate organic phosphorus (g P m⁻³)
- RPOP = refractory particulate organic phosphorus (g P m⁻³)
- APC = phosphorus-to-carbon ratio of all algal groups (g P g⁻¹ C)
- FPD_x = fraction of dissolved organic phosphorus produced by metabolism
- FPL_x = fraction of labile particulate phosphorus produced by metabolism
- FPR_x = fraction of refractory particulate phosphorus produced by metabolism
- FPDP = fraction of dissolved organic phosphorus produced by predation
- FPLP = fraction of labile particulate phosphorus produced by predation
- FPRP = fraction of refractory particulate phosphorus produced by predation

The sums of the metabolism and respiration fractions must each be less than or equal to unity.

Effect of Algae on Nitrogen. Algae take up ammonium and nitrate during production and release ammonium and organic nitrogen through mortality. Nitrate is internally reduced to ammonium before biomass synthesis occurs (Parsons, et al., 1984). Trace concentrations of ammonium inhibit nitrate reduction so that, in the presence of ammonium and nitrate, ammonium is utilized first. The preference of algae for ammonium can be expressed empirically (Thomann and Fitzpatrick, 1982):

$$\begin{aligned} \text{PN}_x = & \text{NH}_4 \frac{\text{NO}_3}{(\text{KH}_{\text{nx}} + \text{NH}_4)(\text{KH}_{\text{nx}} + \text{NO}_3)} \\ & + \text{NH}_4 \frac{\text{KH}_{\text{nx}}}{(\text{NH}_4 + \text{NO}_3)(\text{KH}_{\text{nx}} + \text{NO}_3)} \end{aligned} \quad (\text{A-25})$$

where

$$PN_x = \text{algal preference for ammonium uptake } (0 \leq PN_x \leq 1)$$

The ammonium preference function has two limiting values. When nitrate is absent, the preference for ammonium is unity. When ammonium is absent, the preference is zero. In the presence of ammonium and nitrate, the preference depends on the abundance of both forms relative to the half-saturation constant for nitrogen uptake. When both ammonium and nitrate are abundant, the preference for ammonium approaches unity. When ammonium is scarce but nitrate is abundant, the preference decreases in magnitude and a significant fraction of algal nitrogen comes from nitrate.

Algal nitrogen releases by metabolism and predation are represented by distribution coefficients. The effects of algae on the nitrogen state variables are expressed as:

$$\frac{\delta}{\delta t} NH_4 = (BM_x FNI_x + PR_x FNIP - PN_x P_x) ANC_x B_x \quad (A-26)$$

$$\frac{\delta}{\delta t} NO_3 = (PN_x - 1) P_x ANC_x B_x \quad (A-27)$$

$$\frac{\delta}{\delta t} DON = (BM_x FND_x + PR_x FNDP) ANC_x B_x \quad (A-28)$$

$$\frac{\delta}{\delta t} LPON = (BM_x FNL_x + PR_x FNLP) ANC_x B_x \quad (A-29)$$

$$\frac{\delta}{\delta t} RPON = (BM_x FNR_x + PR_x FNRP) ANC_x B_x \quad (A-30)$$

where

- DON = dissolved organic nitrogen concentration (g N m⁻³)
- LPON = labile particulate organic nitrogen concentration (g N m⁻³)
- RPON = refractory particulate organic nitrogen concentration (g N m⁻³)
- ANC_x = nitrogen-to-carbon ratio of algae (g N g⁻¹ C)
- FNI_x = fraction of inorganic nitrogen produced by metabolism
- FND_x = fraction of dissolved organic nitrogen produced by metabolism

FNLx = fraction of labile particulate nitrogen produced by metabolism
 FNRx = fraction of refractory particulate nitrogen produced by metabolism
 FNIP = fraction of inorganic nitrogen produced by predation
 FNDP = fraction of dissolved organic nitrogen produced by predation
 FNLP = fraction of labile particulate nitrogen produced by predation
 FNRP = fraction of refractory particulate nitrogen produced by predation

The sums of the metabolism fractions and the predation fractions must each equal unity.

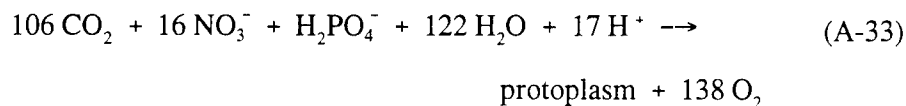
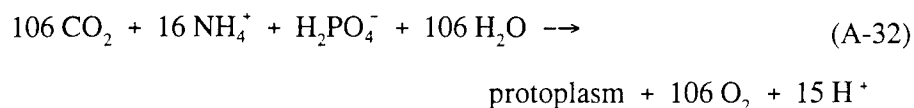
Algal Stoichiometry. Algal biomass is quantified in units of carbon. In order to express the effects of algae on nitrogen and phosphorus, the ratios of nitrogen-to-carbon and phosphorus-to-carbon in algal biomass must be specified. Global mean values of these ratios are well known (Redfield, et al., 1966). Algal composition is known to vary as a function of nutrient availability. As nitrogen and phosphorus become scarce, algae adjust their composition so that smaller quantities of these nutrients are required to produce carbonaceous biomass (Droop, 1973; DiToro, 1980; Parsons et al., 1984). The ratio is described by an empirical approximation:

$$APC = \frac{1}{PCprm1 + PCprm2 e^{-PCprm3 PO_4d}} \quad (A-31)$$

where

PCprm1 = minimum carbon-to-phosphorus ratio (g C g⁻¹ P)
 PCprm2 = difference between minimum and maximum carbon-to-phosphorus ratio (g C g⁻¹ P)
 PCprm3 = effect of dissolved phosphate concentration on carbon-to-phosphorus ratio (m³ g⁻¹ P)

Effect of Algae on Dissolved Oxygen. Algae produce oxygen during photosynthesis and consume oxygen through respiration. The quantity produced depends on the form of nitrogen utilized for growth. More oxygen is produced, per unit of carbon fixed, when nitrate is the algal nitrogen source than when ammonium is the source. Equations describing algal uptake of carbon and nitrogen and production of dissolved oxygen (Morel, 1983) are:



When ammonium is the nitrogen source, one mole of oxygen is produced per mole of carbon dioxide fixed. When nitrate is the nitrogen source, 1.3 moles oxygen are produced per mole of carbon dioxide fixed.

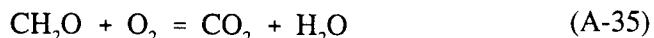
The equation that describes the effect of algae on dissolved oxygen is:

$$\frac{\delta}{\delta t} \text{ DO} = \left[(1.3 - 0.3 \text{ PN}_x) \text{ P}_x - \frac{\text{DO}}{\text{KH}_{\text{rx}} + \text{DO}} \text{ BM}_x \right] \text{ AO CR B}_x \quad (\text{A-34})$$

where

AO CR = dissolved oxygen-to-carbon ratio in respiration (2.67 g O₂ g⁻¹ C)

The magnitude of AO CR is derived from a simple representation of the respiration process:



The quantity (1.3 - 0.3 PN_x) is the photosynthesis ratio and expresses the molar quantity of oxygen produced per mole of carbon fixed. The photosynthesis ratio approaches unity as the algal preference for ammonium approaches unity.

Organic Carbon

Organic carbon undergoes numerous transformations in the water column. The model carbon cycle consists of the following:

- Phytoplankton production
- Phytoplankton exudation
- Predation on phytoplankton
- Dissolution of particulate carbon
- Heterotrophic respiration
- Denitrification

Settling

Algal production is the primary carbon source although carbon also enters the system through external loadings. Predation of algae releases particulate and dissolved organic carbon to the water column. A fraction of the particulate organic carbon undergoes first-order dissolution to dissolved organic carbon. The remainder settles to the sediments. Dissolved organic carbon produced by phytoplankton exudation, predation, and dissolution is respired or denitrified as a first-order rate. No carbon is recycled from the sediments to the water column although oxygen demand created by carbon diagenesis is included in the model.

Dissolution and Respiration Rates. Dissolution and respiration rates depend on the availability of carbonaceous substrate and on heterotrophic activity. Heterotrophic activity and biomass have been correlated with algal activity and biomass across a wide range of natural systems (Bird and Kalff, 1984; Cole, et al., 1988). Consequently, algal biomass can be incorporated into dissolution and respiration rate formulations as a surrogate for heterotrophic activity. The correlation between algae and heterotrophs occurs because algae produce labile carbon that fuel heterotrophic activity. Dissolution and respiration processes do not require the presence of algae and may be fueled entirely by external carbon inputs. Representation of dissolution and respiration in the model allows specification of algal-dependent and algal-independent rates:

$$K_{doc} = K_{dc} + K_{dcalg} \sum_{x=c,d,g} B_x \quad (A-36)$$

where

- K_{doc} = dissolved organic carbon respiration rate (day^{-1})
- K_{dc} = minimum respiration rate (day^{-1})
- K_{dcalg} = constant that relates respiration to algal biomass ($\text{m}^3 \text{g}^{-1} \text{C day}^{-1}$)

$$K_{lpoc} = K_{lc} + K_{lcalg} \sum_{x=c,d,g} B_x \quad (A-37)$$

where

- K_{lpoc} = labile particulate organic carbon dissolution rate (day^{-1})
- K_{lc} = minimum dissolution rate (day^{-1})
- K_{lcalg} = constant that relates dissolution to algal biomass ($\text{m}^3 \text{g}^{-1} \text{C day}^{-1}$)

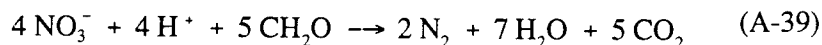
$$K_{rpoc} = K_{rc} + K_{rcalg} \sum_{x=c,d,g} B_x \quad (A-38)$$

where

- K_{rpoc} = refractory particulate organic carbon dissolution rate (day^{-1})
- K_{rc} = minimum dissolution rate (day^{-1})
- K_{rcalg} = constant that relates dissolution to algal biomass ($\text{m}^3 \text{g}^{-1} \text{C day}^{-1}$)

An exponential function relates dissolution and respiration to temperature.

Denitrification. As oxygen is depleted from natural systems, oxidation of organic matter is effected by the reduction of alternate oxidants (referred to as "alternate electron acceptors"). The sequence in which alternate acceptors are employed is determined by the thermodynamics of oxidation-reduction reactions. The first substance reduced in the absence of oxygen is nitrate. A representation of the denitrification reaction can be obtained by balancing standard half-cell redox reactions (Stumm and Morgan, 1981):



Equation A-39 describes the stoichiometry of the denitrification reaction. The kinetics in the model are first-order. The dissolved organic carbon respiration rate, K_{doc} , is modified so that significant decay via denitrification occurs only when nitrate is freely available and dissolved oxygen is depleted. A parameter is included so that the anoxic respiration rate is slower than oxic respiration:

$$\text{Denit} = \frac{K_{Hodoc}}{K_{Hodoc} + \text{DO}} \frac{\text{NO}_3}{K_{Hndn} + \text{NO}_3} \text{AANOX } K_{doc} \quad (A-40)$$

where

- Denit = dissolved organic carbon denitrification rate (day^{-1})
- AANOX = ratio of denitrification to oxic carbon respiration rate ($0 \leq \text{AANOX} \leq 1$)
- K_{Hodoc} = dissolved oxygen half-saturation concentration required for oxic respiration ($\text{g O}_2 \text{m}^{-3}$)
- K_{Hndn} = nitrate half-saturation concentration required for denitrification (g N m^{-3})

An exponential function relates denitrification to temperature. Parameter values in the function are the same as for dissolved organic carbon respiration.

Dissolved Organic Carbon. The complete representation of all dissolved organic carbon sources and sinks in the model is given by:

$$\begin{aligned} \frac{\delta}{\delta t} \text{DOC} = \sum_{x=c,d,g} \left[\left[\text{FCD}_x + (1 - \text{FCD}_x) \frac{\text{KH}_{rx}}{\text{KH}_{rx} + \text{DO}} \right] \text{BM}_x + \text{FCDP PR}_x \right] \text{B}_x \\ + \text{Klpoc LPOC} + \text{Krpoc RPOC} - \frac{\text{DO}}{\text{KH}_{\text{doc}} + \text{DO}} \text{Kdoc DOC} \\ - \text{Denit DOC} \end{aligned} \quad (\text{A-41})$$

Labile Particulate Organic Carbon. The complete representation of all labile particulate organic carbon sources and sinks in the model ecosystem is given by:

$$\frac{\delta}{\delta t} \text{LPOC} = \sum_{x=c,d,g} \text{FCLP PR}_x \text{B}_x - \text{Klpoc LPOC} - \text{WSI} \frac{\delta}{\delta z} \text{LPOC} \quad (\text{A-42})$$

where

$$\text{WSI} = \text{labile particulate settling velocity (m day}^{-1}\text{)}$$

Refractory Particulate Organic Carbon. The complete representation of all refractory particulate organic carbon sources and sinks in the model ecosystem is given by:

$$\frac{\delta}{\delta t} \text{RPOC} = \sum_{x=c,d,g} \text{FCRP PR}_x \text{B}_x - \text{Krpoc RPOC} - \text{WSr} \frac{\delta}{\delta z} \text{RPOC} \quad (\text{A-43})$$

where

$$\text{WSr} = \text{refractory particulate settling velocity (m day}^{-1}\text{)}$$

Phosphorus

The model phosphorus cycle includes the following processes:

- Algal production and metabolism
- Predation
- Hydrolysis of particulate organic phosphorus
- Mineralization of dissolved organic phosphorus
- Settling
- Exchange with inorganic solids

External loads provide the ultimate source of phosphorus to the system. Dissolved phosphate is incorporated by algae during growth and released as phosphate and organic phosphorus through respiration and predation. A portion of the particulate organic phosphorus hydrolyzes to dissolved organic phosphorus. The balance settles to the sediments. Dissolved organic phosphorus is mineralized to phosphate. A portion of the phosphate sorbs to inorganic solids and settles to the sediments. Within the sediments, particulate phosphorus is mineralized and recycled to the water column as dissolved phosphate.

Effects on phosphorus of algal production, metabolism, and predation have already been detailed. Descriptions of hydrolysis and mineralization and of the total phosphate system follow.

Hydrolysis and Mineralization. In the model, hydrolysis is defined as the process by which particulate organic substances are converted to dissolved organic form. Mineralization is defined as the process by which dissolved organic substances are converted to dissolved inorganic form. Conversion of particulate organic phosphorus to phosphate proceeds through hydrolysis and mineralization. Direct mineralization of particulate organic phosphorus does not occur.

Mineralization of organic phosphorus is mediated by the release of nucleotidase and phosphatase enzymes by bacteria (Ammerman and Azam, 1985; Chrost and Overbeck, 1987) and algae (Matavulj and Flint, 1987; Chrost and Overbeck, 1987; Boni, et al., 1989). Since the algae themselves release the enzyme and since bacterial abundance is related to algal biomass, the rate of organic phosphorus mineralization in the model is related to algal biomass. A remarkable property of the enzyme process is that alkaline phosphatase activity is inversely proportional to phosphate concentration (Chrost and Overbeck, 1987; Boni, et al., 1989). Put in different terms, when phosphate is scarce, algae stimulate production of an enzyme that mineralizes organic phosphorus to phosphate. This phenomenon is simulated by relating mineralization to the algal phosphorus nutrient limitation. Mineralization is highest when algae are strongly phosphorus limited and is least when no limitation occurs.

Expressions for mineralization and hydrolysis rates are:

$$K_{dop} = K_{dp} + \frac{K_{Hp}}{K_{Hp} + PO_4d} K_{dpalg} \sum_{x=c,d,g} B_x \quad (A-44)$$

where

- K_{dop} = dissolved organic phosphorus mineralization rate (day^{-1})
- K_{dp} = minimum mineralization rate (day^{-1})
- K_{Hp} = mean half-saturation constant for algal phosphorus uptake = $(K_{Hpc} + K_{Hpd} + K_{Hpg})/3$ ($g\ P\ m^{-3}$)
- K_{dpalg} = constant that relates mineralization to algal biomass ($m^3\ g^{-1}\ C\ day^{-1}$)

$$K_{lpop} = K_{lp} + \frac{K_{Hp}}{K_{Hp} + PO_4d} K_{lpalg} \sum_{x=c,d,g} B_x \quad (A-45)$$

where

- K_{lpop} = labile particulate phosphorus hydrolysis rate (day^{-1})
- K_{lp} = minimum hydrolysis rate (day^{-1})
- K_{lpalg} = constant that relates hydrolysis to algal biomass ($m^3\ g^{-1}\ C\ day^{-1}$)

$$K_{rpop} = K_{rp} + \frac{K_{Hp}}{K_{Hp} + PO_4d} K_{rpalg} \sum_{x=c,d,g} B_x \quad (A-46)$$

where

- K_{rpop} = refractory particulate phosphorus hydrolysis rate (day^{-1})
- K_{rp} = minimum hydrolysis rate (day^{-1})
- K_{rpalg} = constant that relates hydrolysis to algal biomass ($m^3\ g^{-1}\ C\ day^{-1}$)

An exponential function relates mineralization and hydrolysis rates to temperature.

When the nutrient concentration greatly exceeds the half-saturation concentration for algal uptake, the rate roughly equals the minimum. Algal biomass has little influence. As phosphorus becomes scarce relative to the half-saturation concentration, the rate increases. The magnitude of increase depends on algal biomass.

The Total Phosphate System. One fraction of total phosphorus in the water column is phosphorus incorporated in algal biomass. This fraction is computed in the model as the product of algal biomass and APC, the phosphorus-to-carbon ratio. In the environment, algae adjust their phosphorus content in re-

sponse to external conditions. Algal phosphorus content is high when external phosphorus is abundant and phosphorus content is low when phosphorus is scarce. The adaptation of algae to their environment indicates the phosphorus-to-carbon ratio should be a variable in the model. However, treatment of the ratio as a variable greatly complicates computation of phosphorus transport due to the mixture of algal masses of different composition. The complication is avoided if intracellular and extracellular phosphorus are treated and transported as a single state variable. Intracellular and extracellular concentrations are determined by equilibrium partitioning of their sum.

Adsorption is the process in which ions or molecules are attracted to the surface of a solid. Phosphate ions exhibit a strong adsorption to particulate species of metals including iron and manganese. Particulate and dissolved fractions are determined by equilibrium partitioning of their sum.

The model phosphate state variable is defined as the sum of dissolved phosphate, sorbed phosphate, and algal phosphorus content as:

$$PO_4t = PO_4d + PO_4p + PO_4a \quad (A-47)$$

where

$$\begin{aligned} PO_4t &= \text{total phosphate (g P m}^{-3}\text{)} \\ PO_4d &= \text{dissolved phosphate (g P m}^{-3}\text{)} \\ PO_4p &= \text{particulate (sorbed) phosphate (g P m}^{-3}\text{)} \\ PO_4a &= \text{algal phosphorus (g P m}^{-3}\text{)} \end{aligned}$$

Exchange With Particulate Metals. Detailed treatment of iron and manganese is not included in the model. Instead, the state variable total active metal is defined as the sum of all metals that act as sorption sites. Phosphate sorbs only to the particulate fraction of the total metal. Therefore, the total metal is partitioned into particulate and dissolved fractions via an equilibrium partition coefficient. Extracellular phosphate is partitioned by a linear sorption isotherm so that dissolved and particulate fractions are computed as:

$$PO_{4d} = \frac{1}{1 + Kadpo4 TAMp} (PO_{4t} - PO_{4a}) \quad (A-48)$$

$$PO_{4p} = \frac{Kadpo4 TAMp}{1 + Kadpo4 TAMp} (PO_{4t} - PO_{4a}) \quad (A-49)$$

where

$Kadpo4$ = sorbed vs. dissolved phosphate partition coefficient ($m^3 \text{ mol}^{-1}$)

$TAMp$ = particulate total active metal ($\text{mol } m^{-3}$)

Computation of Algal Phosphorus. Algal phosphorus is defined as:

$$PO_{4a} = APC \sum_{x=c,d,g} Bx \quad (A-50)$$

The phosphorus-to-carbon ratio is calculated by the empirical function expressed in Equation A-31.

The equations 4-31, A-48, A-49, A-50, form an implicit system. The implicit nature of the system can be seen by substituting the expressions for dissolved phosphate (Equation A-48) and algal phosphate (Equation A-50) into the expression for phosphorus-to-carbon ratio (Equation A-31):

$$APC = \frac{1}{PCprm1 + PCprm2 e^{-PCprm3 (PO_{4a} - APC \sum Bx)}} \quad (A-51)$$

The phosphorus-to-carbon ratio appears on both sides of the equation and cannot be obtained explicitly. (For simplicity, $Kadpo4 = 0$ in this example.) Within the model code, the phosphorus-to-carbon ratio is obtained by iterative solution of Equation A-51 in each control volume. From the phosphorus-to-carbon ratio, algal phosphorus is computed (Equation A-50). Next, extracellular phosphate is partitioned into dissolved and particulate fractions (Eqs. A-48 and A-49).

Phosphate. Once the interactions of dissolved, particulate, and algal phosphate are made explicit, the balance of the equations describing phosphorus are straightforward summations of previously-described sources and sinks:

$$\frac{\delta}{\delta t} \text{PO}_4^t = - \sum_{x=c,d,g} \text{WS}_x \frac{\delta}{\delta z} \text{APC B}_x - \text{WS}_s \frac{\delta}{\delta z} \text{PO}_4^p + \text{Kdop DOP} \quad (\text{A-52})$$

where

WS_s = particulate metal settling velocity (m day⁻¹)

Algal uptake and release of phosphate represents an exchange of phosphate fractions rather than a phosphate source or sink. Consequently, no algal source or sink terms are included in the phosphate mass-conservation equation. The settling terms are required to represent the settling of particulate phosphate incorporated in algal biomass or sorbed to particles.

Dissolved Organic Phosphorus.

$$\begin{aligned} \frac{\delta}{\delta t} \text{DOP} = & \sum_{x=c,d,g} (\text{BM}_x \text{FPD}_x + \text{PR}_x \text{FPDP}) \text{APC B}_x \\ & + \text{Klpop LPOP} + \text{Krpop RPOP} - \text{Kdop DOP} \end{aligned} \quad (\text{A-53})$$

Labile Particulate Organic Phosphorus.

$$\begin{aligned} \frac{\delta}{\delta t} \text{LPOP} = & \sum_{x=c,d,g} (\text{BM}_x \text{FPL}_x + \text{PR}_x \text{FPLP}) \text{APC B}_x \\ & - \text{Klpop LPOP} - \text{WSl} \frac{\delta}{\delta z} \text{LPOP} \end{aligned} \quad (\text{A-54})$$

Refractory Particulate Organic Phosphorus.

$$\begin{aligned} \frac{\delta}{\delta t} \text{RPOP} = & \sum_{x=c,d,g} (\text{BM}_x \text{FPR}_x + \text{PR}_x \text{FPRP}) \text{APC B}_x \\ & - \text{Krpop RPOP} - \text{WSr} \frac{\delta}{\delta z} \text{RPOP} \end{aligned} \quad (\text{A-55})$$

Nitrogen

The model nitrogen cycle includes the following processes:

- Algal production and metabolism
- Predation
- Hydrolysis of particulate organic nitrogen
- Mineralization of dissolved organic nitrogen
- Settling
- Nitrification
- Denitrification

External loads provide the ultimate source of nitrogen to the system. Inorganic nitrogen is incorporated by algae during growth and released as ammonium and organic nitrogen through respiration and predation. A portion of the particulate organic nitrogen hydrolyzes to dissolved organic nitrogen. The balance settles to the sediments. Dissolved organic nitrogen is mineralized to ammonium. In an oxygenated water column, a fraction of the ammonium is subsequently oxidized to nitrate. In anoxic water, nitrate is lost to nitrogen gas through denitrification. Particulate nitrogen that settles to the sediments is mineralized and recycled to the water column, primarily as ammonium. Nitrate moves in both directions across the sediment-water interface, depending on relative concentrations in the water column and sediment interstices.

Effects on nitrogen of algal production, metabolism, and predation have already been detailed. Descriptions of hydrolysis, mineralization, nitrification and denitrification follow.

Hydrolysis and Mineralization. In the model, particulate organic nitrogen is converted to dissolved organic nitrogen via hydrolysis. Dissolved organic nitrogen is converted to ammonium through mineralization. Conversion of particulate nitrogen to ammonium proceeds through hydrolysis and mineralization. Direct mineralization of particulate nitrogen does not occur. The argument for accelerated hydrolysis and mineralization during nutrient-limited conditions is not as clear for nitrogen as for phosphorus. However, the same formulations are made available for nitrogen as for phosphorus. Accelerated processes can be activated or deactivated through parameter selection. The nitrogen hydrolysis and mineralization formulations are:

$$K_{don} = K_{dn} + \frac{K_{Hn}}{K_{Hn} + NH_4 + NO_3} K_{dnalg} \sum_{x=c,d,g} B_x \quad (A-56)$$

where

- K_{don} = dissolved organic nitrogen mineralization rate (day^{-1})
- K_{dn} = minimum mineralization rate (day^{-1})
- K_{Hn} = algal nitrogen uptake mean half-saturation constant = $(K_{Hnc} + K_{Hnd} + K_{Hng})/3$ ($g\ N\ m^{-3}$)
- K_{dnalg} = constant that relates mineralization to algal biomass ($m^3\ g^{-1}\ C\ day^{-1}$)

$$K_{lpon} = K_{ln} + \frac{K_{Hn}}{K_{Hn} + NH_4 + NO_3} K_{lnalg} \sum_{x=c,d,g} B_x \quad (A-57)$$

where

- K_{lpon} = labile particulate nitrogen hydrolysis rate (day^{-1})
- K_{ln} = minimum hydrolysis rate (day^{-1})
- K_{lnalg} = constant that relates hydrolysis to algal biomass ($m^3\ g^{-1}\ C\ day^{-1}$)

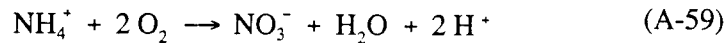
$$K_{rpon} = K_{rn} + \frac{K_{Hn}}{K_{Hn} + NH_4 + NO_3} K_{rinalg} \sum_{x=c,d,g} B_x \quad (A-58)$$

where

- K_{rpon} = refractory particulate nitrogen hydrolysis rate (day^{-1})
- K_{rn} = minimum hydrolysis rate (day^{-1})
- K_{rinalg} = constant that relates hydrolysis to algal biomass ($m^3\ g^{-1}\ C\ day^{-1}$)

An exponential function relates mineralization and hydrolysis rates to temperature.

Nitrification. Nitrification is a process mediated by specialized groups of autotrophic bacteria that obtain energy through the oxidation of ammonium to nitrite and oxidation of nitrite to nitrate. A simplified expression for complete nitrification (Tchobanoglous and Schroeder, 1987) is:



The equation indicates that two moles of oxygen are required to nitrify one mole of ammonium into nitrate. However, the simplified equation is not strictly true. Cell synthesis by nitrifying bacteria is accomplished by the fixation of

carbon dioxide so that less than two moles of oxygen are consumed per mole ammonium utilized (Wezernak and Gannon, 1968).

The kinetics of complete nitrification are modeled as a function of available ammonium, dissolved oxygen, and temperature:

$$NT = \frac{DO}{KH_{ont} + DO} \frac{NH_4}{KH_{nnt} + NH_4} f(T) NT_m \quad (A-60)$$

where

- NT = nitrification rate (g N m⁻³ day⁻¹)
- KH_{ont} = dissolved oxygen half-saturation constant required for nitrification (g O₂ m⁻³)
- KH_{nnt} = NH₄ half-saturation constant required for nitrification (g N m⁻³)
- NT_m = maximum nitrification rate at optimal temperature (g N m⁻³ day⁻¹)

The kinetics formulation incorporates the products of two Monod functions. The first function diminishes nitrification at low dissolved oxygen concentration. The second function expresses the influence of ammonium concentration on nitrification. When ammonium concentration is low, relative to KH_{nnt}, nitrification is proportional to ammonium concentration. For NH₄ < KH_{nnt}, the reaction is approximately first-order. (The first-order decay constant ≈ NT_m/KH_{nnt}.) When ammonium concentration is large relative to KH_{nnt}, nitrification approaches a maximum rate. This formulation is based on a concept proposed by Tuffey, et al. (1974). Nitrifying bacteria adhere to benthic or suspended sediments. When ammonium is scarce, vacant surfaces suitable for nitrifying bacteria exist. As ammonium concentration increases, bacterial biomass increases, vacant surfaces are occupied, and the rate of nitrification increases. The bacterial population attains maximum density when all surfaces suitable for bacteria are occupied. At this point, nitrification proceeds at a maximum rate independent of additional increase in ammonium concentration.

The optimal temperature for nitrification may be less than peak temperatures that occur in coastal waters. To allow for a decrease in nitrification at superoptimal temperature, the effect of temperature on nitrification is modeled in the Gaussian form of Equation A-14.

Effect of Nitrification on Ammonium.

$$\frac{\delta}{\delta t} \text{NH}_4 = - \text{NT} \quad (\text{A-61})$$

Effect of Nitrification on Nitrate.

$$\frac{\delta}{\delta t} \text{NO}_3 = \text{NT} \quad (\text{A-62})$$

Effect of Nitrification on Dissolved Oxygen.

$$\frac{\delta}{\delta t} \text{DO} = - \text{AONT NT} \quad (\text{A-63})$$

where

AONT = mass dissolved oxygen consumed per mass ammonium-nitrogen nitrified ($4.33 \text{ g O}_2 \text{ g}^{-1} \text{ N}$)

Effect of Denitrification on Nitrate. The effect of denitrification on dissolved organic carbon has been described. Denitrification removes nitrate from the system in stoichiometric proportion to carbon removal as determined by Equation A-39:

$$\frac{\delta}{\delta t} \text{NO}_3 = - \text{ANDC Denit DOC} \quad (\text{A-64})$$

where

ANDC = mass nitrate-nitrogen reduced per mass dissolved organic carbon oxidized ($0.933 \text{ g N g}^{-1} \text{ }^\circ\text{C}$)

Nitrogen Mass Balance Equations. The mass-balance equations for nitrogen state variables are written by summing all previously-described sources and sinks:

Ammonium.

$$\frac{\delta}{\delta t} \text{NH}_4 = \sum_{x=c,d,g} (\text{BM}_x \text{FNI}_x + \text{PR}_x \text{FNIP} - \text{PN}_x \text{Px}) \text{ANC}_x \text{B}_x \quad (\text{A-65})$$

$$+ \text{Kdon DON} - \text{NT}$$

Dissolved Organic Nitrogen.

$$\frac{\delta}{\delta t} \text{DON} = \sum_{x=c,d,g} (\text{BM}_x \text{FND}_x + \text{PR}_x \text{FNDP}) \text{ANC}_x \text{B}_x \quad (\text{A-66})$$

$$+ \text{Klpon LPON} + \text{Krpon RPON} - \text{Kdon DON}$$

Labile Particulate Organic Nitrogen.

$$\frac{\delta}{\delta t} \text{LPON} = \sum_{x=c,d,g} (\text{BM}_x \text{FNL}_x + \text{PR}_x \text{FNL P}) \text{ANC}_x \text{B}_x \quad (\text{A-67})$$

$$- \text{Klpon LPON} - \text{WSl} \frac{\delta}{\delta z} \text{LPON}$$

Refractory Particulate Organic Nitrogen.

$$\frac{\delta}{\delta t} \text{RPON} = \sum_{x=c,d,g} (\text{BM}_x \text{FNR}_x + \text{PR}_x \text{FNR P}) \text{ANC}_x \text{B}_x \quad (\text{A-68})$$

$$- \text{Krpon RPON} - \text{WSr} \frac{\delta}{\delta z} \text{RPON}$$

Nitrate.

$$\frac{\delta}{\delta t} \text{NO}_3 = \sum_{x=c,d,g} (\text{PN}_x - 1) \text{Px} \text{ANC}_x \text{B}_x \quad (\text{A-69})$$

$$+ \text{NT} - \text{ANDC Denit DOC}$$

Silica

The model incorporates two siliceous state variables, available silica and particulate biogenic silica. For practical purposes, available silica is equivalent to dissolved silica although sorption of available silica to inorganic solids occurs. The silica cycle is a simple one in which diatoms take up available silica and recycle available and particulate biogenic silica through the actions of metabo-

lism and predation. Particulate silica dissolves in the water column or settles to the bottom. A portion of the settled particulate biogenic dissolves within the sediments and returns to the water column as available silica. Sources and sinks represented are:

- Diatom production and metabolism
- Predation
- Dissolution of particulate to dissolved silica
- Settling
- Exchange with inorganic solids

Available Silica. Dissolved silica sorb to newly-formed metal particles and rapidly settled to the bottom. To represent this process, available silica is partitioned into dissolved and particulate fractions according to a linear sorption isotherm:

$$SAd = \frac{1}{1 + Kadsa TAMp} SA \quad (A-70)$$

$$SAp = \frac{Kadsa TAMp}{1 + Kadsa TAMp} SA \quad (A-71)$$

where

- SA = available silica concentration (g Si m⁻³)
- SAd = dissolved available silica (g Si m⁻³)
- SAp = particulate available silica (g Si m⁻³)
- Kadsa = partition coefficient of sorbed vs. dissolved available silica (m³ mol⁻¹)

The kinetic equation for available silica is:

$$\frac{\delta}{\delta t} SA = (FSAP PRd - Pd) ASCd Bd - WSs \frac{\delta}{\delta z} SAp + Ksua SU \quad (A-72)$$

where

- SU = particulate biogenic silica concentration (g Si m⁻³)
- FSAP = fraction of diatom silica made available by predation (0 ≤ FSAP ≤ 1)
- ASCd = silica-to-carbon ratio of diatoms (g Si g⁻¹ C)
- Ksua = particulate silica dissolution rate (day⁻¹)

Particulate Biogenic Silica. The kinetic equation for particulate biogenic silica is:

$$\frac{\delta}{\delta t} \text{SU} = (\text{BMd} + (1 - \text{FSAP}) \text{PRd}) \text{ASCd Bd} - \text{WSs} \frac{\delta}{\delta z} \text{SU} \quad (\text{A-73})$$

$$- \text{KSUA SU}$$

An exponential function describes the effect of temperature on silica dissolution.

Chemical Oxygen Demand

In the model, chemical oxygen demand is the concentration of reduced substances that are oxidizable through inorganic means. The source of chemical oxygen demand in saline water is sulfide released from sediments. A cycle occurs in which sulfate is reduced to sulfide in the sediments and reoxidized to sulfate in the water column. In freshwater, methane is released to the water column by the sediment model. Both sulfide and methane are quantified in units of oxygen demand and are treated with the same kinetic formulation:

$$\frac{\delta}{\delta t} \text{COD} = - \frac{\text{DO}}{\text{KHocod} + \text{DO}} \text{Kcod COD} \quad (\text{A-74})$$

where

COD = chemical oxygen demand concentration (g O₂-equivalents m⁻³)

KHocod = half-saturation concentration of dissolved oxygen required for exertion of chemical oxygen demand (g O₂ m⁻³)

Kcod = oxidation rate of chemical oxygen demand (day⁻¹)

An exponential function describes the effect of temperature on exertion of chemical oxygen demand.

Dissolved Oxygen

Sources and sinks of dissolved oxygen in the water column include:

- Algal photosynthesis
- Atmospheric reaeration
- Algal respiration
- Heterotrophic respiration
- Nitrification
- Chemical oxygen demand

Reaeration. The rate of reaeration is proportional to the dissolved oxygen deficit in model segments that form the air-water interface:

$$\frac{\delta}{\delta t} DO = \frac{K_r}{\Delta z} (DO_s - DO) \quad (A-75)$$

where

K_r = reaeration coefficient ($m \text{ day}^{-1}$)
 DO_s = dissolved oxygen saturation concentration ($g \text{ O}_2 \text{ m}^{-3}$)

The surface renewal concept, attributed to Danckwerts by O'Connor and Dobbins (1958), indicates:

$$K_r = \sqrt{Dl R} \quad (A-76)$$

where

Dl = molecular diffusivity of oxygen in water ($\approx 1.7 \times 10^{-4} \text{ m}^2 \text{ day}^{-2}$)
 R = surface renewal rate (day^{-1})

Specification of the surface renewal rate is the fundamental problem in reaeration theory. O'Connor and Dobbins (1958) state that, in isotropic turbulence, surface renewal can be approximated as the ratio of stream velocity to depth. The renewal rate is also influenced by wind (O'Connor, 1983). Influences of temperature (ASCE, 1961) and salinity (Wen, et al., 1984) on aeration, most likely effected through changes in diffusivity, have been measured. No single theory that unites all these factors into a formulation of reaeration in an estuary is available. The surface renewal concept is retained with the renewal rate treated as a calibration parameter.

Saturation dissolved oxygen concentrations decrease as temperature and salinity increase. An empirical formula that describes these effects (Genet, et al., 1974) is:

$$\begin{aligned} DO_s = & 14.5532 - 0.38217 T + 0.0054258 T^2 \\ & - (1.665 \times 10^{-4} - 5.866 \times 10^{-6} T + 9.796 \times 10^{-8} T^2) CL \end{aligned} \quad (A-77)$$

where

CL = chloride concentration ($= \text{salinity}/1.80655$)

Summary of Dissolved Oxygen Sources and Sinks. The complete kinetics for dissolved oxygen are:

$$\begin{aligned} \frac{\delta}{\delta t} DO = & \sum_{x=c,d,g} \left[(1.3 - 0.3 PN_x) P_x - \frac{DO}{KH_{rx} + DO} BM_x \right] AOCR B_x \\ & - AONT NT - \frac{DO}{KH_{doc} + DO} AOCR K_{doc} DOC \\ & - \frac{DO}{KH_{cod} + DO} K_{cod} COD + \frac{K_r}{\Delta z} (DO_s - DO) \end{aligned} \quad (A-78)$$

Total Active Metal

The total active metal state variable is the sum of iron and manganese concentrations. Iron and manganese exist in particulate and dissolved forms in estuaries. The prime determinant of the species is dissolved oxygen. In the oxygenated water, total iron and manganese are almost completely particulate. Under anoxic conditions, large fractions of total iron and manganese are dissolved although solid-phase sulfides and carbonates exist and may predominate. The simplified partitioning of particulate and dissolved phases of total active metal employed here notes that total active metal concentration must achieve a minimum level before precipitation occurs. The minimum level is a function of dissolved oxygen:

$$TAM_d = \text{minimum} (TAM_{dmx} e^{-K_{dotam} DO}, TAM) \quad (A-79)$$

$$TAM_p = TAM - TAM_d \quad (A-80)$$

where

- TAM = total active metal concentration (mol m⁻³)
- TAM_d = dissolved total active metal (mol m⁻³)
- TAM_p = particulate total active metal (mol m⁻³)
- TAM_{dmx} = solubility of total active metal under anoxic conditions (mol m⁻³)
- K_{dotam} = constant that relates total active metal solubility to dissolved oxygen concentration (m³ g⁻¹ O₂)

The origin of total active metal in the model is benthic sediments. Since metal release is not explicit in the sediment model, release is incorporated into the kinetics portion of the water-column model. Release is treated as a spatially-uniform, empirical function of temperature and dissolved oxygen concentration.

The only other source or sink in the water column is settling of the particulate fraction. In the mass balance equation, the benthic source operates only in model cells that adjoin the bottom:

$$\frac{\delta}{\delta t} \text{TAM} = - \text{WSs} \frac{\delta}{\delta z} \text{TAMp} + \frac{\text{KHbmf}}{\text{KHbmf} + \text{DO}} \frac{\text{BENTAM}}{\Delta z} \quad (\text{A-81})$$

where

BENTAM = anoxic total active metal release rate (mol m⁻² day⁻¹)

KHbmf = dissolved oxygen concentration at which total active metal release is half the anoxic rate (g O₂ m⁻³)

Release of metal from the bottom is maximum when dissolved oxygen is absent from the overlying water. Release declines as oxygen concentration increases and is negligible when dissolved oxygen >> KHbmf.

Sediment release of total active metal is treated as an exponential function of temperature.

Salinity

No internal sources or sinks of salinity exist.

Temperature

The only source or sink of internal energy considered is exchange with the atmosphere. Although solar radiation can penetrate several meters into the water column, radiation-induced increases in internal energy are assigned entirely to the surface model layer.

The internal-energy equation can be written as a conservation of temperature equation. Change in temperature due to atmospheric exchange is considered proportional to the temperature difference between the water surface and a theoretical equilibrium temperature (Edinger, et al., 1965):

$$\frac{\delta}{\delta t} T = \frac{KT}{\rho C_p \Delta z} (T_e - T) \quad (\text{A-82})$$

where

Te = equilibrium temperature ($^{\circ}\text{C}$)
KT = Heat exchange coefficient ($\text{W m}^{-2} \text{ }^{\circ}\text{C}^{-1}$)
Cp = specific heat of water ($4200 \text{ W sec kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$)
 ρ = density of water (1000 kg m^{-3})

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